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02280.002660.

## PATENT APPLICATION

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re A	Application of	)	
		:	Examiner: S. Gollamudi
NURE	IAN PINAR TÜTÜNCÜ ET AL.	)	
		:	Group Art Unit: 1616
Applic	cation No.: 09/825,992	)	_
		:	
Filed:	April 5, 2001	)	
		:	
For:	CONFECTIONERY PRODUCT	)	
	HAVING A SALIVATION REGION	:	
	AND AN ORAL COMFORT REGION	)	

Commissioner for Patents P. O. Box 1450 Alexandria, Virginia 22313-1450

## **DECLARATION OF KEVIN STANTON**

- I, Kevin Stanton, declare and say that:
- I am a Product Development Manager and Senior Process
   Development Engineer at Masterfoods USA and have been in this position since 1998.
- 2. I graduated from University of California, Davis, with a Master of Science degree in Agricultural Engineering and I have worked in the field of food product development for 16 years.
- 3. I am one of the named inventors on the above-identified application.

- 4. I have read the Office Action, dated December 29, 2005, in the above-identified application (hereinafter the "Office Action") and I have read the prior art cited in the Office Action and referenced in the statements herein.
- 5. I understand that the Office Action, at page 5, asserts that U.S. Patent No. 6,231,900 (hereinafter "Hanke") teaches a composition containing an "orange flavor". I further understand that the Office Action asserts that this ingredient contains orange oil, which is an "essential oil" and that this ingredient is alleged to correspond to or "read on" an oral comfort ingredient selected from the group consisting of lipids, surfactants and mixtures thereof in an amount effective to lubricate, coat or moisten an oral cavity.
- 6. Lipids, as that term would be understood by one of ordinary skill in the art, generally refers to glycerol esters of fatty acids, which account for ninety-nine percent of lipids of plant and animal origin. See the attached excerpt from Owen R. Fennema, Ed., *Food Chemistry*, Marcel Dekker, Inc. (New York) (1985), p.140.
- 7. That general understanding is reinforced in the context of the specification of the invention where the lipids that are given as examples are all triacylglycerides, including partially hydrogenated palm kernel oil, medium chain triglycerides, coconut oil, anhydrous milk fat, cocoa butter, corn oil, palm oil, soybean oil, sunflower oil, canola oil and mixtures thereof (see paragraph [0032] of the present application).
- 8. "Essential oils" do not contain glycerol esters of fatty acids, which are what one of ordinary skill would associate with the word "oils." Rather, essential oils contain a variety of terpenes and oxygenated derivatives, including alcohols, aldehydes,

ketones and esters. Thus, the Examiner is incorrect that an orange oil is a lipid as that term is correctly understood in the context of the specification of the invention.

- 9. I am familiar with orange flavor and orange oil, and such ingredients are irritants, and they would not have the effect of lubricating, coating or moistening the oral cavity.
- oil, a copy of which is attached hereto, would prevent the ordinarily skilled artisan from using this ingredient to lubricate, coat or moisten the oral cavity. See, for example, Section 3 of the MSDS, where the irritant effects of this ingredient are clearly identified. The Examiner's assertion that an essential oil would be used as an oral comfort ingredient is clearly in error since used in the amounts called for in the present invention, essential oils would be irritant and not oral comfort ingredients.
- 11. I do not believe that one of ordinary skill in the art would consider "orange oil" to fall within "the group consisting of lipids, surfactants and mixtures thereof," as that phrase would be understood by one of ordinary skill in the art, reading the specification of the present invention.
- 12. Xerostomia, or dry mouth, is a condition in which insufficient saliva is created in the mouth.
- 13. The product covered by the pending claims of the subject application was developed at least in part to alleviate xerostomia.
- 14. Certain claims in the subject application specifically recite a method of treating xerostomia.

- 15. I understand that the Office Action at pages 6 to 7 states that

  Hanke teaches "administering a confectionery product comprising two distinct areas of
  an oral comforting region and a salivation region to the oral cavity to the same population
  (those with throat irritation, which is a symptom of xerostomia)."
- 16. The symptoms of cough and cold, including sore throat, are distinct from the symptoms of xerostomia. Sore throat due to cough and cold is generally caused by infection or allergic reaction in the throat, and the symptoms are treated by treating the throat. The symptoms of xerostomia arise from having insufficient saliva in the mouth, and the symptoms are treated by treating the mouth.
- 17. One of ordinary skill in the art would recognize that administering a soothing composition to the throat of a person suffering from cough and cold symptoms is distinct from administering a salivation agent to the mouth of a person suffering from xerostomia, and that these do not constitute "the same population."
- 18. For at least the foregoing reasons, Hanke does not teach an oral comfort region, a confectionery containing an oral comfort region and a salivation region, or a method of treating xerostomia with such a confectionery.
- 19. I have read International Application No. WO 99/59427 (hereinafter "Le"), and I do not understand Le to teach or suggest the concentration of acidulent in a macroscopic region of a confectionery product.
- 20. I have read U.S. Patent No. 5,284,659 (hereinafter "Cherukuri") and I do not understand Cherukuri to teach the use of acidulents at all, and I especially do not understand that reference to teach or suggest the concentration of acidulent in a macroscopic region of a confectionery product.

- 21. I do not understand Cherukuri to contain any teaching relevant to promoting salivation.
- 22. I do not find teaching or suggestion in either Le or Cherukuri that would lead one of ordinary skill in the art to substitute an acidulent, such as taught in Le page 5, lines 13 to 22 for the breath deodorant taught in Cherukuri Table II.
- 23. For at least the foregoing reasons, I do not consider that it would have been "obvious" in view of Cherukuri and Le to formulate a product having two discrete regions, wherein acidulent is concentrated in one region in an amount effective to enhance salivation, and wherein an oral comfort ingredient selected from lipids, surfactants and mixtures thereof, is concentrated in the other of the two regions.
- 24. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Subscribed this  $f^{5t}$  day of  $f^{5t}$ , 2006.

Kevin Stanton

Kens Krondon the

NY\_Main 562821\_1





Health	2
Fire	- 2
	• <del>• • • •</del>
Reactivity	U
Personal Protection	Н

# Material Safety Data Sheet Orange oil, Sweet MSDS

## **Section 1: Chemical Product and Company Identification**

Product Name: Orange oil, Sweet

Catalog Codes: SLO1006

CAS#: 8028-48-6 or 8008-57-9

**RTECS: RI8600000** 

TSCA: TSCA 8(b) inventory: Orange oil, Sweet

CI#: Not available.

Synonym: Oil of Sweet Orange

Chemical Name: Orange Oil

Chemical Formula: Not available.

**Contact Information:** 

Sciencelab.com, Inc. 14025 Smith Rd. Houston, Texas 77396

US Sales: 1-800-901-7247

International Sales: 1-281-441-4400

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:

1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

## Section 2: Composition and Information on Ingredients

#### Composition:

Name	CAS#	% by Weight
Orange oil, Sweet	8028-48-6 or	100
	8008-57-9	

**Toxicological Data on Ingredients:** Orange oil, Sweet: ORAL (LD50): Acute: >5000 mg/kg [Rat]. DERMAL (LD50): Acute: >5000 mg/kg [Rabbit].

## **Section 3: Hazards Identification**

#### **Potential Acute Health Effects:**

Hazardous in case of skin contact (irritant), of eye contact (irritant). Slightly hazardous in case of skin contact (permeator), of ingestion, of inhalation.

## **Potential Chronic Health Effects:**

CARCINOGENIC EFFECTS: Not available.
MUTAGENIC EFFECTS: Not available.
TERATOGENIC EFFECTS: Not available.
DEVELOPMENTAL TOXICITY: Not available.

Repeated or prolonged exposure is not known to aggravate medical condition.

## Section 4: First Aid Measures

## **Eye Contact:**

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention.

#### **Skin Contact:**

In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.

#### **Serious Skin Contact:**

Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.

#### Inhalation:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

#### Serious Inhalation:

Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention.

#### Ingestion:

Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

## Section 5: Fire and Explosion Data

Flammability of the Product: Flammable.

Auto-Ignition Temperature: Not available.

Flash Points: CLOSED CUP: 46.111°C (115°F).

Flammable Limits: Not available.

Products of Combustion: Not available.

#### Fire Hazards in Presence of Various Substances:

Flammable in presence of open flames and sparks, of heat.

Non-flammable in presence of shocks.

### **Explosion Hazards in Presence of Various Substances:**

Risks of explosion of the product in presence of mechanical impact: Not available.

Risks of explosion of the product in presence of static discharge: Not available.

## **Fire Fighting Media and Instructions:**

Flammable liquid, insoluble in water.

SMALL FIRE: Use DRY chemical powder.

LARGE FIRE: Use water spray or fog. Cool containing vessels with water jet in order to prevent pressure

build-up, autoignition or explosion.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

## Section 6: Accidental Release Measures

Small Spill: Absorb with an inert material and put the spilled material in an appropriate waste disposal.

## Large Spill:

Flammable liquid, insoluble in water.

Keep away from heat. Keep away from sources of ignition. Stop leak if without risk. Absorb with DRY earth, sand or other non-combustible material. Do not get water inside container. Do not touch spilled material. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal.

## Section 7: Handling and Storage

#### **Precautions:**

Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe gas/fumes/ vapor/spray. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents.

## Storage:

Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame). Sensitive to light. Store in light-resistant containers.

## Section 8: Exposure Controls/Personal Protection

## **Engineering Controls:**

Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work-station location.

#### Personal Protection:

Splash goggles. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

## Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

## Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid.

Odor: Characteristic. (Strong.)

Taste: Characteristic.

Molecular Weight: Not available.

Color: Yellow. Orange. Deep Orange

pH (1% soln/water): Not applicable.

Boiling Point: Not available.

Melting Point: Not available.

Critical Temperature: Not available.

Specific Gravity: 0.844 (Water = 1)

Vapor Pressure: 0.1 kPa (@ 20°C)

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: Not available.

Solubility: Insoluble in cold water.

## Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Heat, ignition sources, light, incompatible materials

Incompatibility with various substances: Reactive with oxidizing agents.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity: Sensitive to light.

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

## Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Eye contact.

**Toxicity to Animals:** 

Acute oral toxicity (LD50): >5000 mg/kg [Rat].

Acute dermal toxicity (LD50): >5000 mg/kg [Rabbit].

Chronic Effects on Humans: Not available.

Other Toxic Effects on Humans:

Hazardous in case of skin contact (irritant).

Slightly hazardous in case of skin contact (permeator), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

**Special Remarks on other Toxic Effects on Humans:** 

Acute Potential Health Effects:

Liquid is irritating to eyes and skin. It may also be irritating to the respiratory tract and digestive tract.

## Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

**Products of Biodegradation:** 

Possibly hazardous short term degradation products are not likely. However, long term degradation products may

arise.

Toxicity of the Products of Biodegradation: Not available.

Special Remarks on the Products of Biodegradation: Not available.

## **Section 13: Disposal Considerations**

## Waste Disposal:

Waste must be disposed of in accordance with federal, state and local environmental control regulations.

## **Section 14: Transport Information**

DOT Classification: CLASS 3: Flammable liquid.

Identification: : Extracts, Flavoring, Liquid (Orange Oil) UNNA: 1197 PG: III

Special Provisions for Transport: Not available.

## **Section 15: Other Regulatory Information**

Federal and State Regulations: TSCA 8(b) inventory: Orange oil, Sweet

Other Regulations:

OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).

EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

## Other Classifications:

## WHMIS (Canada):

CLASS B-3: Combustible liquid with a flash point between 37.8°C (100°F) and 93.3°C (200°F).

## DSCL (EEC):

R10- Flammable.

R36/38- Irritating to eyes and skin.

S16- Keep away from sources of ignition - No

smoking.

S24/25- Avoid contact with skin and eyes.

S36/37/39- Wear suitable protective clothing.

gloves and eve/face protection.

## HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 2

Reactivity: 0

Personal Protection: h

National Fire Protection Association (U.S.A.):

Health: 2

Flammability: 2

Reactivity: 0

Specific hazard:

**Protective Equipment:** 

Gloves.
Lab coat.
Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate.
Splash goggles.

## Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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## FOOD CHEMISTRY

SECOND EDITION, REVISED AND EXPANDED

Edited by Owen R. Fennema

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## LIPIDS

Wassef W. Nawar University of Massachusetts, Amherst, Massachusetts

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#### I. INTRODUCTION

Lipids consist of a broad group of compounds that are generally soluble in organic solvents but only sparingly soluble in water. They are major components of adipose tissue, and together with proteins and carbohydrates, they constitute the principal structural components of all living cells. Glycerol esters of fatty acids, which make up to 99% of the lipids of plant and animal origin, have been traditionally called fats and oils. Based solely on whether the material is solid or liquid at room temperature, distinction between a fat and an oil is of little practical importance, and the two terms are often used interchangeably.

Food lipids are either consumed in the form of "visible" fats, which have been separated from the original plant or animal source, for example, butter, lard, shortening, or salad oils, or as constituents of basic foods, such as milk, cheese, or meat. The largest supply of vegetable oil comes from the seeds of soybean, cottonseed, and peanut, and the oil-bearing trees of palm, coconut, and olive.

Lipids in food exhibit unique physical and chemical properties. The composition, crystalline structure, melting and solidifying behavior, and association with water and other nonlipid molecules are especially important with regard to the various textural properties they impart, and to their functionality in bakery and confectionary products and in many other products that are cooked. They undergo complex chemical changes and react with other food constituents, producing numerous compounds both desirable and deleterious to food quality.

Dietary lipids play an important role in nutrition. They supply calories and essential fatty acids, act as vitamin carriers, and increase the palatability of food, but for decades they have been at the center of controversy with respect to toxicity and disease.

#### II. NOMENCLATURE

Lipid nomenclature can be understood more readily if simple nomenclature of the various classes of organic compounds, as covered in most texts of organic chemistry, is reviewed first. Updated recommendations for the nomenclature of lipids have been recently reviewed (50).

## A. Fatty Acids

This term refers to any aliphatic monocarboxylic acid that can be liberated by hydrolysis from naturally occurring fats.

$$CH_{2}OOC (CH_{2})_{16} CH_{3}$$

$$CH_{3} (CH_{2})_{7} CH = CH (CH_{2})_{7} COOCH$$

$$CH_{2}OOC (CH_{2})_{12} CH_{3}$$

and would be designated 1-stearoyl-2-oleoyl-3-myristoyl-sn-glycerol, sn-glycerol-1-stearate-2-oleate-3-myristate, sn-StOM, or sn-18:0-18:1-16:0.

The following prefixes are now widely used with abbreviations to designate the positional distribution of fatty acids within triacylglycerol molecules.

sn: used immediately preceding the term "glycerol," indicates that the sn-1, sn-2, and sn-3 position are listed in that order.

rac: racemic mixture of two enantiomers. The middle acid in the abbreviation is attached at the sn-2 position, but the remaining two acids are equally divided between sn-1 and sn-3 (e.g., rac-StOM indicates equal amounts of sn-StOM and sn-MOSt).

 $\beta$ : middle acid in the abbreviation is at the sn-2 position but positioning of the remaining two is unknown (e.g.,  $\beta$ -StOM indicates a mixture of sn-StOM and sn-MOSt in any proportion.

No prefix is given in case of monoacid acylglycerols (e.g., MMM) or if the positional distribution of the acids is unknown, and hence any mixture of isomers is possible (e.g., StOM indicates a possible mixture of sn-StOM, sn-MOSt, sn-OStM, sm-MStO, sn-StMO, and sn-OMSt in any proportion).

## C. Phospholipids

The term "phospholipid" may be used for any lipid containing phosphoric acid as a mono- or diester. "Glycerophospholipid" signifies any derivative of glycerophosphoric acid that contains an O-acyl, O-alkyl, or O-alkenyl group attached to the glycerol residue. The common glycerophospholipids are named as derivatives of phosphatidic acid, such as 3-sn-phosphatidylcholine (trivial name, lecithin), or by their systematic name, similar to the system for triacylglycerols. The term "phospho" is used to indicate the phosphodiester bridge; for example, 1-palmitoyl-2-linoleyl-sn-glycero-3-phosphocholine is the designation for the compound

$$\begin{array}{c} \text{CH}_2\text{OOC} \left( \text{ CH}_2 \right)_{14} \text{CH}_3 \\ \\ \text{CH}_3 \left( \text{CH}_2 \right)_4 \text{CH} = \text{CHCH}_2 \text{CH} = \text{CH} \left( \text{CH}_2 \right)_7 \text{COOCH} \\ \\ \\ \text{CH}_2 \text{O-P-O-} \left( \text{CH}_2 \right)_2 \overset{\dagger}{\text{N}} \left( \text{CH}_3 \right)_3 \\ \\ \\ \text{O} \end{array}$$

## III. CLASSIFICATION

A general classification of lipids based on their structural components is presented in Table 2. Such a classification, however, may be too rigid for a group of compounds so di-

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and myristic

Table 2 Classification of Lipids

Major class	Subclass	Description
Simple lipids	Acylglycerols Waxes	Glycerol + fatty acids Long-chain alcohol + long-chain fatty acid
Compound lipids	Phosphoacylglycerols (or glycerophospholipids)	Glycerol + fatty acids + phosphate + another group usually con- taining nitrogen
	Sphingomyelins	Sphingosine + fatty acid + phosphate + choline
	Cerebrosides	Sphingosine + fatty acid + simple sugar
	Gangliosides	Sphingosine + fatty acid + complex carbohydrate moiety that includes sialic acid
Derived lipids	Materials that meet the definition of a lipid but are not simple or compound lipids	Examples: carotenoids, steroids, fat-soluble vitamins

verse as lipids, and should be used only as a guide. It also should be recognized that other classifications sometimes may be more useful. For example, the phosphoacylglycerols and the sphingomyelins can be classed as phospholipids because of the presence of phosphate. Similarly, the cerebrosides and the gangliosides also can be classed as glycolipids because of the presence of carbohydrate, and the sphingomyelins and the glycolipids also can be classed as sphingolipids because of the presence of sphingosine.

The most abundant class of food lipids is the acylglycerols, which dominate the composition of animal or vegetable fats and oils. Acylglycerols are traditionally classified into the following subgroups.

#### A. Milk Fats

Fats of this group are derived from the milk of ruminants, particularly dairy cows. Although the major fatty, acids of milk fat are palmitic, oleic, and stearic, this fat is unique among animal fats in that it contains appreciable amounts of the shorter chain acids C4 to C12, and small amounts of branched and odd-numbered acids.

#### B. Lauric Acids

Fats of this group are derived from certain species of palm, such as coconut and babasu. The fats are characterized by their high content of lauric acid (40-50%), moderate amounts of C6, C8, and C10 fatty acids, low content of unsaturated acids, and their relatively low melting points.

## C. Vegetable Butters

Fats of this group are derived from the seeds of various tropical trees and are distinguished by their narrow melting range, which is mainly due to the arrangement of fatty

2-t-6-c-NONADIENAL

2-t-6-c-NONADIENOL

Figure 12 Conversion of aldehyde to alcohol resulting in subtle flavor modifications in cucumbers and melons.

## F. Volatiles from Branched-Chain Amino Acids

Branched-chain amino acids serve as important flavor precursors for the biosynthesis of compounds associated with the ripening of some fruits. Bananas and apples are particularly good examples of this process because much of the ripe flavor of each of these fruits is caused by volatiles from amino acids (20,97). The initial reaction involved in this flavor formation (Fig. 14) is sometimes referred to as enzymic Strecker degradation because transamination and decarboxylation occur that parallel those occurring during nonenzymic browning. Several microorganisms, including yeast and malty flavor-producing strains of Streptococcus lactis, can also modify most of the amino acids in a fashion similar to that shown in Fig. 14. Plants can also produce similar derivatives from amino acids other than leucine, and the occurrence of 2-phenethanol with a rose or lilaclike aroma in blossoms is attributed to these reactions.

Although the aldehydes, alcohols, and acids from these reactions contribute directly to the flavors of ripening fruits, the esters are the dominant character-impact compounds. It has long been known that isomyl acetate is important in banana flavor, but other compounds are also required to give full banana flavors. Ethyl 2-methylbutyrate is even more applelike than ethyl-3-methylbutyrate (Fig. 14), and the former compound is the dominant note in the aroma of ripe Delicious apples.

#### G. Volatile Terpenoids in Flavors

Because of the abundance of terpenes in plant materials used in the essential oil and perfumery industries, their importance in other plant-associated flavors is sometimes underestimated. They are largely responsible, however, for the flavors of citrus fruits and many

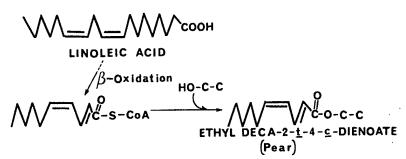


Figure 13 Formation of a key aroma substance in pears through  $\beta$ -oxidation of linoleic acid followed by esterification.

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osynthesis of are particuach of these volved in this gradation beirring during lavor-producs in a fashion from amino e or lilaclike ribute directimpact comna flavor, but thylbutyrate er compound

ul oil and pertimes underits and many

on of linoleic

Figure 14 Enzymic conversion of leucine to volatiles illustrating the aroma compounds formed from amino acids in ripening fruits.

seasonings and herbs. Terpenes are present at low concentrations in a number of fruits and are responsible for much of the flavor of raw carrot roots (13).

Terpenes are biosynthesized through the isoprenoid (C5) paths (Fig. 15). Monoterpenes contain 10 C atoms; the sesquiterpenes contain 15 C atoms (25). Terpenes account for some of the branched alkyl compounds found in natural flavor volatiles, but they also may be converted to ring compounds that can become aromaticized. Cumin aldehyde

Figure 15 Generalized isoprenoid scheme for the biosynthesis of monoterpenes.

(1-formyl-4-isopropylbenzene), which is a strong characterizing compound in cumin spice, is illustrative of an aromatic derivative of terpenes. Essential oils, or flavor extracts containing terpenes, can be separated into nonoxygenated (hydrocarbon) and oxygenated fractions using silicic acid chromatrography and nonpolar and polar solvent elutions, respectively. Oxygenated terpenes frequently exhibit more desirable flavors than do nonoxygenated terpenes, and the former are therefore preferred for some flavor applications. "Terpeneless" orange oil, for example, contains principally the oxygenated terpene fraction from orange oils.

Terpenes frequently possess extremely strong character-impact properties, and they can be easily identified by one experienced with natural product aromas. For example, the monoterpenes, citral (XIX) with limonene (XX), exhibit distinctive aromas of lemons and limes, respectively.

Terpene enantiomers also can exhibit extremely different odor qualities, and the carvones have been studied extensively from this perspective (76). l-Carvone [4(R)(-)carvone] (XXII) possesses a strong, characteristic spearmint aroma; d-carvone [4(S)(+)carvone] (XXI) has the characteristic aroma of caraway spice. Studies on such pairs of compounds are of interest since they provide information on the fundamental process of olfaction and structure-activity relationships for molecules.

$$(4\underline{S})-(+)-CARVONE$$

$$(caraway)$$

$$(XXI)$$

$$(XXII)$$

$$(XXIII)$$

Sesquiterpenes are also important characterizing aroma compounds, with  $\beta$ -sinensal (XXIII) and nootkatone (XXIV) providing characterizing flavors to oranges and grape-fruit, respectively. The diterpenes (C20) are too large and nonvolatile to contribute directly to aromas.

$$\beta \text{-SINENSAL} \\ \text{(orange)} \\ \text{(XXIII)} \\ \text{(XXIV)}$$

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